PROJECT THEMIS RESEARCH REPORT

Report No. 12

June 1970

FERRATE(VI) ANALYSIS BY SPECTROPHOTOMETRY AND VOLTAMMETRY

by

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FERRATE(VI) ANALYSIS BY SPECTROPHOTOMETRY AND VOLTAMMETRY

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ABSTRACT

Spectrophotometric and voltammetric methods were developed for the analysis of potassium ferrate(VI) in dilute solutions, where the standard chromite method is inapplicable. A direct proportionality prevails between the ferrate concentration and the absorbance on the one hand, and the ferrate concentration and the ferrate reduction current on the other. However, voltammetry has greater precision than spectrophotometry in very dilute solutions.

INTRODUCTION

Various aspects of ferrate(VI) chemistry such as its production (chemical[1-5] and electrochemical[5]), stability[6,7], oxidation properties[8] and magnetic properties[9] have been explored for the past several decades. Any such study necessitates the development of a reliable analytical technique capable of reasonable accuracy at low concentrations of ferrate. The very low solubility of potassium ferrate in strongly basic solutions, and its instability, lead to difficulties in the standardization of analytical methods.

Analytical Methods for Ferrate:

Three types of methods for ferrate analysis will be discussed: (a) Chemical, (b) Spectrophotometric, and (c) Electrochemical.

The most reliable of the chemical methods is the chromite method developed by Schreyer and coworkers[10]. This method, based on oxidation of chromium(III) to chromate(VI) by ferrate in strongly alkaline solutions, was found to give low values in very dilute solutions, probably due to incomplete oxidation of chromite. However, consistent results are obtainable for ferrate analysis in solid samples under controlled titration conditions, and this information is necessary for the standardization of the spectrophotometric and the electrochemical methods. Spectrophotometry and voltammetry appeared more promising than the chromite method for ferrate analysis in dilute solutions.

EXPERIMENTAL

EQUIPMENT AND APPARATUS

The instrumentation employed for spectrophotometry was a Bausch and Lomb Spectronic 20; for voltammetry, a Princeton Applied Research Model 170 Electrochemistry System was used.

The electrochemical cell consisted of three compartments, the side compartments, each about 320 ml in volume, being separated from the central compartment (30 ml capacity) by two 1" diameter sintered discs (10-20 μ porosity) situated 2" apart. The central compartment was provided with an inlet and stopper.

Three reference electrodes were tried - saturated calomel, Hg/Hg_2SO_4/Sat K_2SO_4, and Hg/HgO/xN KOH, of which the last was found to be most suitable.

The mercury-mecuric oxide electrode has been described by Ives and Janz[11]. A simple construction of this electrode has been furnished by Thaker[12]. Although considerable use is being made of this reference electrode, as yet no information is available on the effect of hydroxyl-ion concentration on the half-cell potential. The potential for the reaction:

$$Hg + 2\,OH^- = HgO + H_2O + 2e^-$$

is given by

$$E = E^\circ - \frac{RT}{2E} \ln \frac{a_{H_2O}}{a_{OH^-}^2}$$

$$= -0.097 - 0.0295 \log \frac{a_{H_2O}}{a_{OH^-}^2}$$

The potential, therefore, depends upon the activity of water and on the square of the hydroxyl-ion activity. Fig. 1 is a plot of half-cell potential as a function of concentration of potassium hydroxide; potentials are expressed relative to standard hydrogen electrode.

MATERIALS

Potassium Ferrate:

Potassium ferrate, prepared and purified by Gump[7] by the standard method of

Thompson and coworkers[4] was used. This was homogenized by careful grinding. The average analysis by the Schreyer method[10] was 96.1%, which is in good agreement with Gump's value of 95.9%. For some preliminary investigations a sample of 89.6% purity was utilized.

Potassium Hydroxide:

It was noted that there were varying amounts of oxidizable impurities in the 'Baker Analyzed' KOH which was used to prepare solutions of ferrate. Therefore, it was purified by treatment with H_2O_2 (3 lbs. of KOH dissolved in 900 ml water required 50 ml of 30% H_2O_2); the mixture was allowed to react for one hour with intermittent shaking and then boiled for half an hour before testing for the presence of excess H_2O_2 by the starch-iodide method. The alkali was then estimated on a carbonate-free basis as follows: 20 ml of 10% $BaCl_2$ solution was added to 20 ml of approximately $\frac{N}{5}$ KOH to precipitate any carbonate. The mixture was then titrated against standard $\frac{N}{5}$ potassium hydrogen phthalate with phenolphthalein as the indicator. Titrations with and without $BaCl_2$ addition showed the presence of only traces of carbonate in the alkali. Furthermore, a sharp end-point proved that a negligible amount of the borosilicate glass container had dissolved during the preparation of the alkali, which was then stored in polyethylene bottles.

PROCEDURES :

Various concentrations of potassium ferrate ranging from 0.758×10^{-4} to 3.03×10^{-4} mole/l were made by dissolving weighed amounts of analyzed K_2FeO_4 in solutions of KOH which had been previously bubbled with N_2 for one half-hour to remove dissolved oxygen. The dissolution time varied from 5 mins to 35 mins with the strength of potassium hydroxide (from 3N to 14N).

Experiments using spectrophotometry and cyclic voltammetry were run under identical conditions, namely constant temperature of 25°C and under normal fluorescent lighting conditions of the laboratory. The wavelength chosen for spectrophotometry was 500 nm, where the maximum absorption of ferrate ion occurs.

The experimental conditions for cyclic voltammetry were as detailed below:

Scan range: +0.1 to -0.5 V vs. Hg/HgO/10.5N KOH electrode.

Sweep rate: 5 mV/sec

Sensitivity: 50 or 100 μA full scale

Anode: 0.065" diameter iron wire (3" length; purity = 99.7%) with 1/2" coating of pyrex glass 1" from the immersed end.

Cathode: Platinum gauze

Anode electrolyte: 1.515×10^{-4} mole K_2FeO_4 per liter of 10.5N KOH.

Cathode electrolyte: 10.5N KOH

Standard stirring conditions (1800 RPM; lucite stirrer positioned midway between the bottom of the cell and the end of the iron wire electrode).

Low-pass filter position at 30 m. sec.

RESULTS AND DISCUSSION

Spectrophotometry:

(a) Effect of reduction products of ferrate on absorbance:

It was suspected that one of the reduction products likely to affect absorbance is hydrous ferric oxide which precipitates when a solution of ferrate in dilute potassium hydroxide is kept for a long time, or boiled. Ferrate solutions in concentrated potassium hydroxide yield colorless decomposition products.

In order to assess the influence of decomposition products on absorbance, centrifuged and uncentrifuged samples of ferrate were investigated. This showed that the products of decomposition of ferrate had no effect on the absorbance.

(b) Preparation of calibration curve:

The absorbance for 3.03×10^{-4}, 1.515×10^{-4} and 0.758×10^{-4} g/l of potassium ferrate in 14N potassium hydroxide were found to be at 500 nm, in good agreement with the value of 498 nm reported by Schreyer[13] for strongly basic solutions of potassium ferrate. However, a slight shift in the absorbance peak from 500 to 480 nm was observed in 3N and 6N potassium hydroxide solutions for the above ferrate concentrations.

A linear relationship was obtained between the absorbance and the concentration of potassium ferrate over the range 0.253×10^{-4} to 1.768×10^{-4} mole/l. (Fig. 2).

Cyclic Voltammetry:

This technique offers a potential method for ferrate analysis especially useful at low concentrations. Typical voltammograms are shown in Figs. 3-6.

The voltammograms for 10.5N potassium hydroxide are given in Figs. 3(a) and 3(b). The characteristic shape of the voltammogram does not change noticeably with the geometry of the iron anode (0.065" iron wire, 1" depth; or 1/2" x 1/2" Fe sheet, 0.005" thick) nor with variation in potassium hydroxide concentration from 10.5N to 14N. It can be seen that the ferrate reduction wave occurs at -0.15 V vs. Hg/HgO/10.5N KOH.

The reduction wave was confirmed by three different methods:

(a) holding at different potentials in the vicinity of ferrate formation (ca +0.65 V) and sweeping back (Fig. 4).

(b) adding a few drops of ferrate to the solution during the cathodic sweep and observing the increase in the reduction wave (Fig. 5). and

(c) using three different concentrations of ferrate (0.758×10^{-4}, 1.515×10^{-4} and 3.03×10^{-4} mole/l) as the anode electrolyte and comparing the wave heights (Fig. 6).

It can be noted from Fig. 4 that the ferrate reduction wave occurs at -0.3 V vs. Hg/HgO/sat KOH electrode for 3.03×10^{-4} mole/l of potassium ferrate in saturated potassium hydroxide. The wave intensity increases with holding time and with the magnitude of the anodic potential at which the potential is held, reaching a maximum at ca. +0.65 V. In Fig. 5 the height of the ferrate reduction wave (at -0.5 V vs. SCE) increases with the addition of ferrate at the iron electrode. It is of interest to see the direct proportionality between the reduction current and the ferrate concentration in Fig. 6. The increased sensitivity obtainable by stirring the solution is evident; the background current (Fig. 6a) does not increase with stirring.

Preparation of calibration curve:

The relationship between the "ferrate" reduction current (i.e., total reduction current minus the current for background electrolyte) at -0.15 V and the ferrate concentration is linear as is evident from Fig. 7. This calibration curve was prepared starting with 320 ml (volume of one compartment of the cell) of the potassium hydroxide solution and progressively replacing 50 ml of it with an equal volume of 1.515×10^{-4} mole/l stock ferrate solution.

Comparison of electrodes:

The suitability of platinum electrodes (0.025" dia.; 1/2" depth of immersion in solution) in preference to the iron electrode was investigated. While in the case of the iron electrode, the current at -0.15 V vs. Hg/HgO/10.5N KOH electrode for the pure solvent (10.5N potassium hydroxide) is negligibly small, platinum oxide (formed during the anodic sweep using the platinum electrode) is

reduced at nearly the same potential as ferrate and hence might interfere with the analysis, especially at low concentrations of ferrate. Fig. 8 shows that platinum oxide is reduced at about -0.2 V vs. Hg/HgO/10.5N KOH, the reduction wave being intensified by holding for 2 mins at 0.7 V and sweeping back. On prolonged use in concentrated ferrate solutions, the iron electrode becomes coated with ferrate which might interfere with ferrate analysis.

Ferrate reduction can also be observed at a mercury electrode[14] and thus polarography with the dropping mercury electrode would also be a possible analytical technique.

Comparison of techniques:

Spectrophotometry is simple and quick, especially suited for the study of the decomposition of ferrate in concentrated potassium hydroxide which takes more than a day. On the other hand, cyclic voltammetry is considerably more sensitive: While the lower limit of potassium ferrate analysis by spectrophotometry is about 0.25×10^{-4} mole/l in concentrated potassium hydroxide solutions, cyclic voltammetry could be used for analyzing concentrations as low as 0.025×10^{-4} mole/l.

Cyclic voltammetry is dependent on spectrophotometry for calibration purposes. The iron electrode is prone to poisoning on prolonged use; therefore, it is necessary to polish the iron electrode with fine emery paper prior to every run and then to calibrate it with the aid of spectrophotometry.

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FIGURE CAPTIONS

Fig. 1 Effect of concentration of potassium hydroxide on mercury-mercuric oxide electrode potential.

Fig. 2 Relationship between absorbance and concentration of potassium ferrate.

Fig. 3 Typical voltammograms for 10.5N potassium hydroxide using iron wire anode: (a) showing reduction of ferrate at -0.15V, (b) showing ferrate reduction with stirring using higher sensitivity.

Fig. 4 Effect of oxygen evolution and holding time on ferrate reduction.

Fig. 5 Effect of ferrate addition on the waveheight for ferrate reduction.

Fig. 6 Effect of concentration and stirring on ferrate wave.

Fig. 7 Calibration curve for potassium ferrate.

Fig. 8 Voltammogram for 10.5N potassium hydroxide showing reduction of oxide film on platinum electrode at about -0.2V.

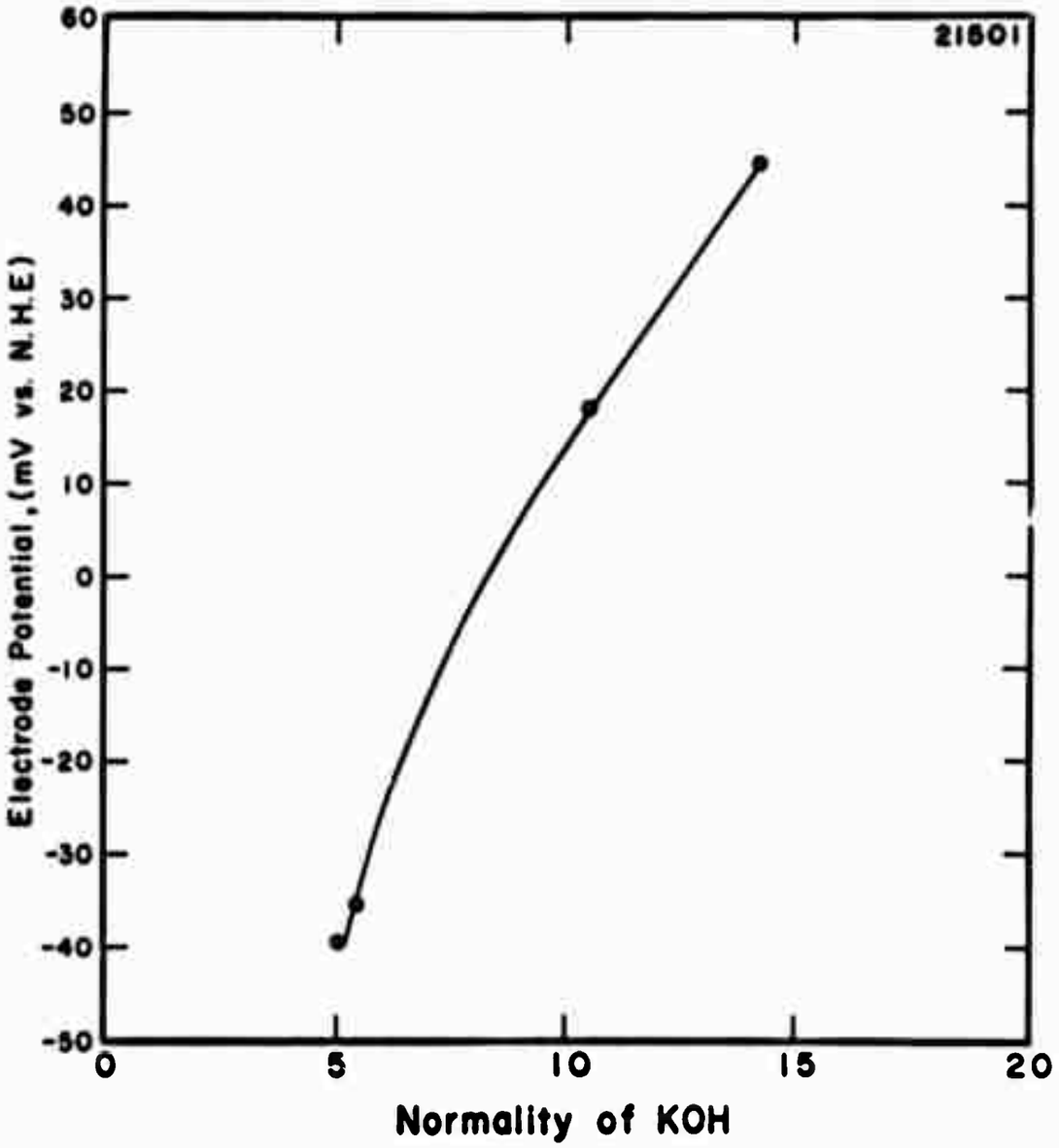

Figure 1. Effect of concentration of potassium hydroxide on mercury-mercuric oxide electrode potential.

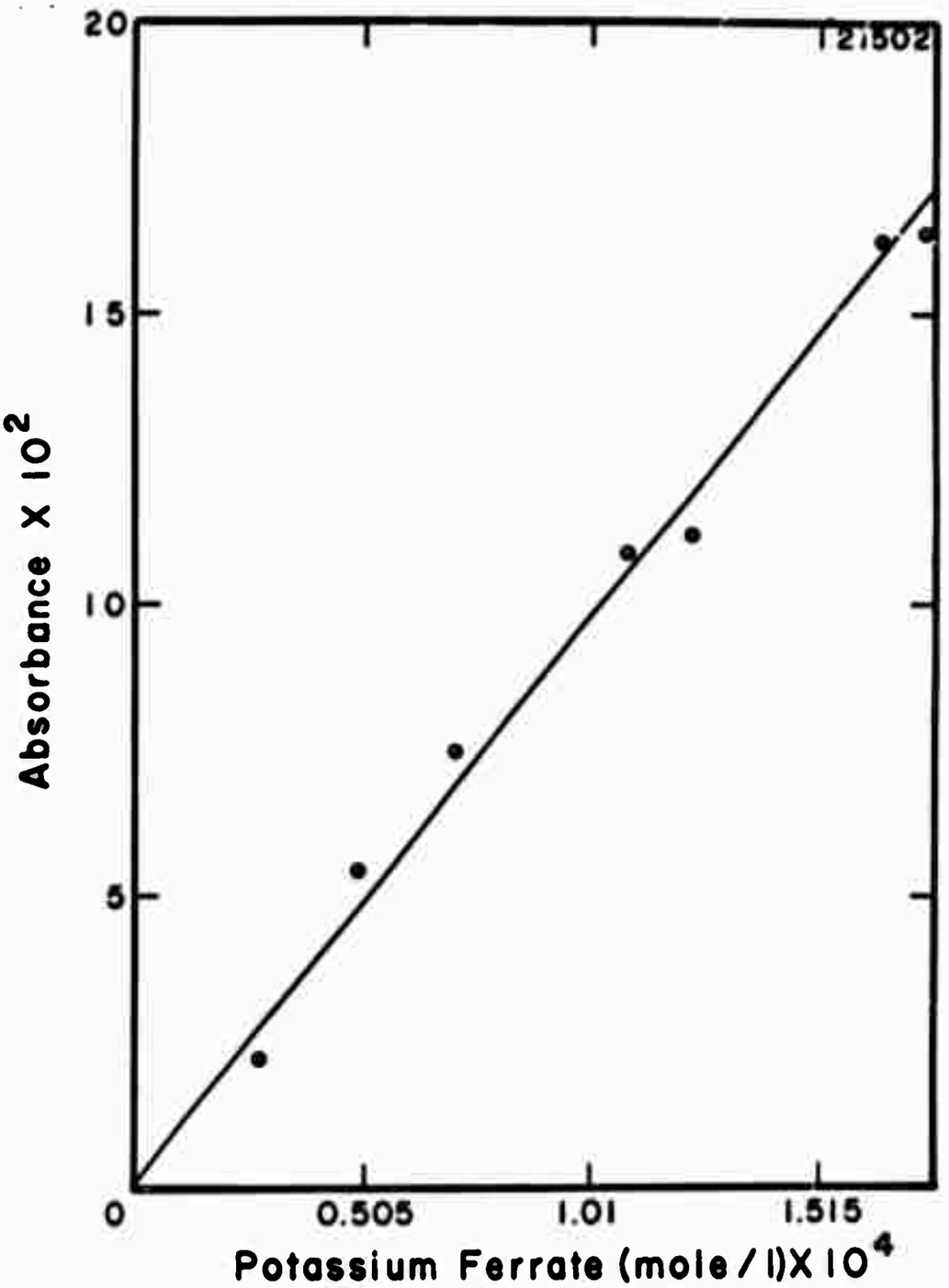

Figure 2. Relationship between absorbance and concentration of potassium ferrate.

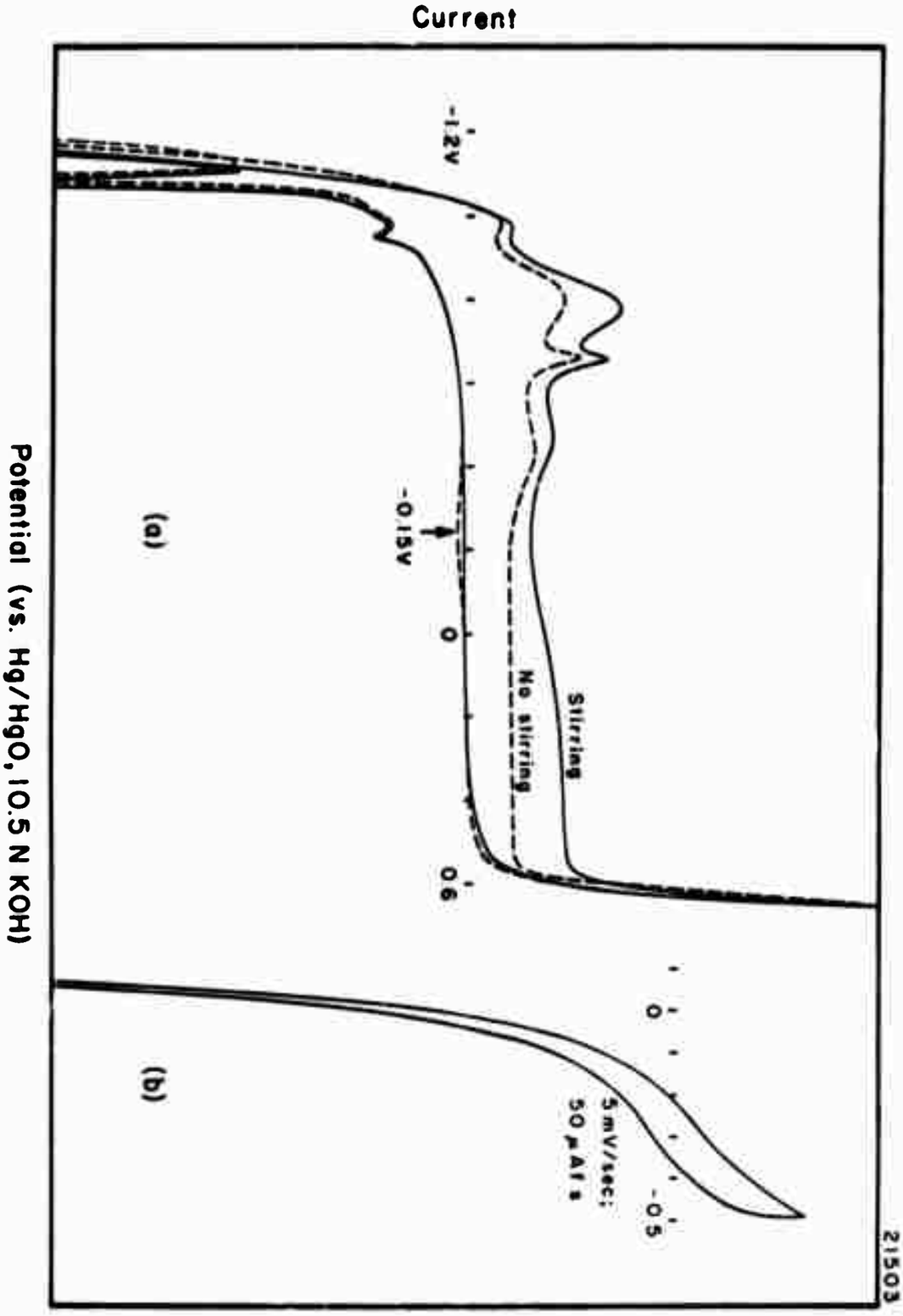

Figure 3. Typical voltammograms for 10.5N potassium hydroxide using iron wire anode: (a) showing reduction of ferrate at -0.15V, (b) showing ferrate reduction with stirring using higher sensitivity.

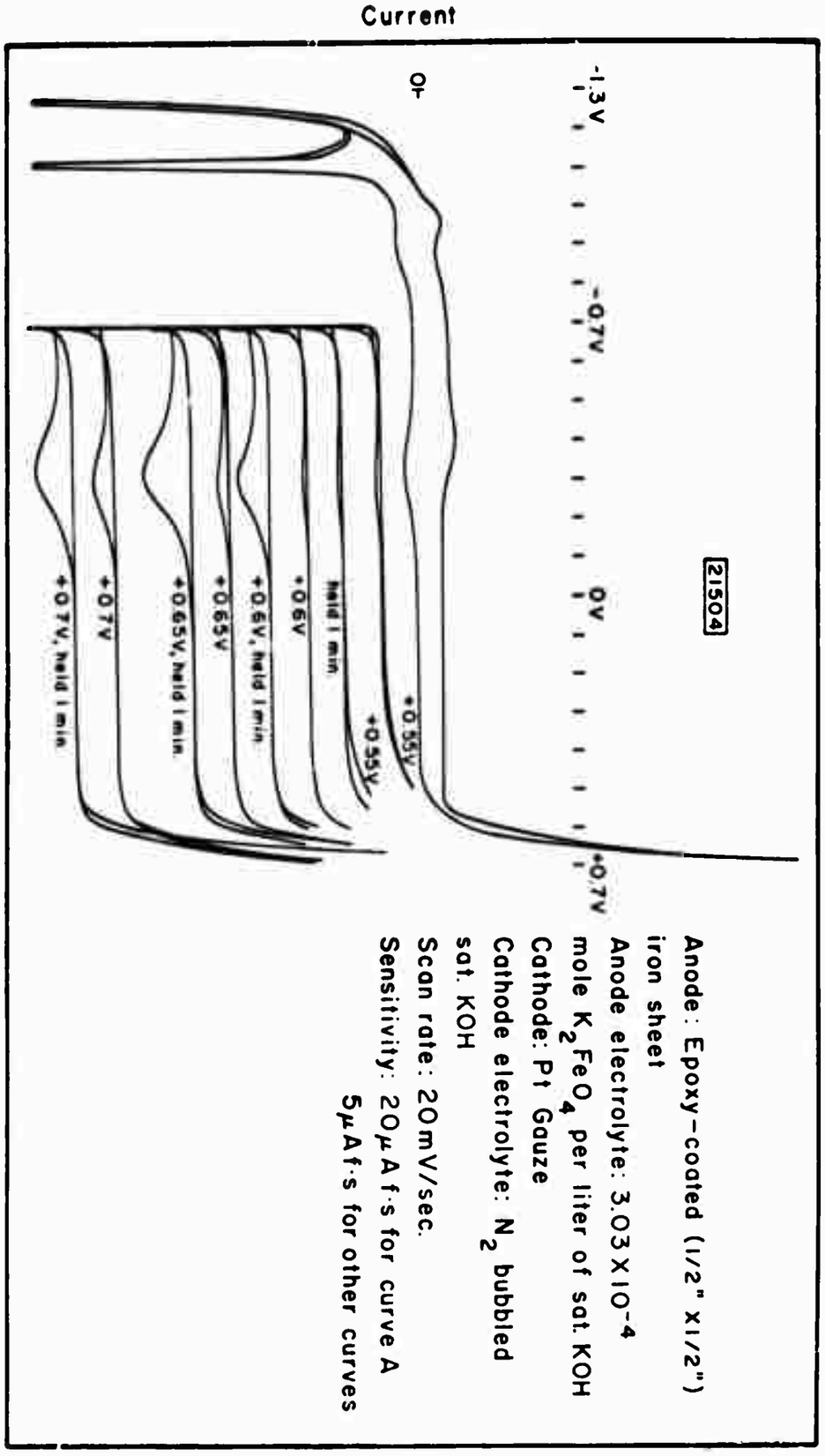

Figure 4. Effect of oxygen evolution and holding time on ferrate reduction.

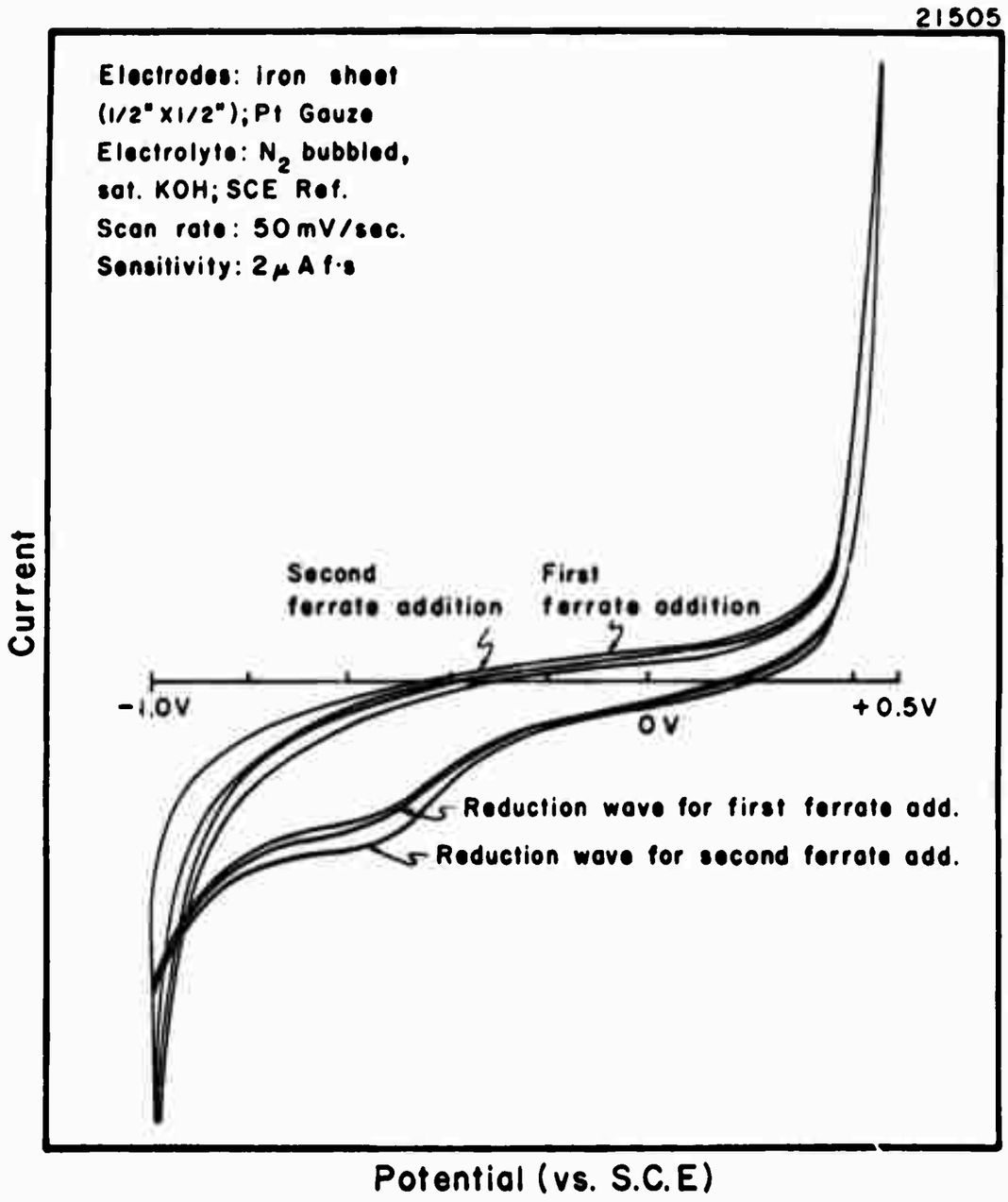

Figure 5. Effect of ferrate addition on the waveheight for ferrate reduction.

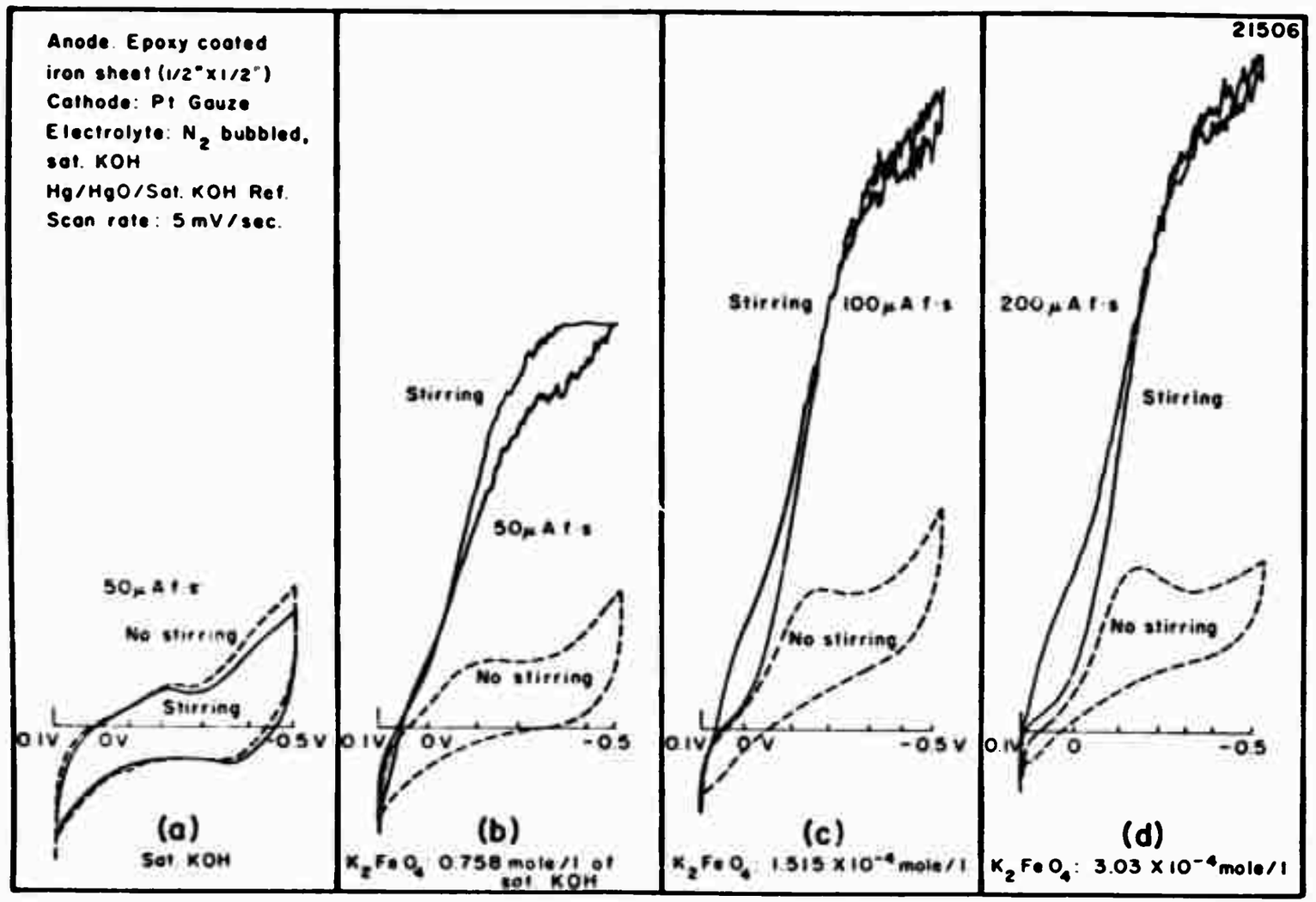

Figure 6. Effect of concentration and stirring on ferrate wave.

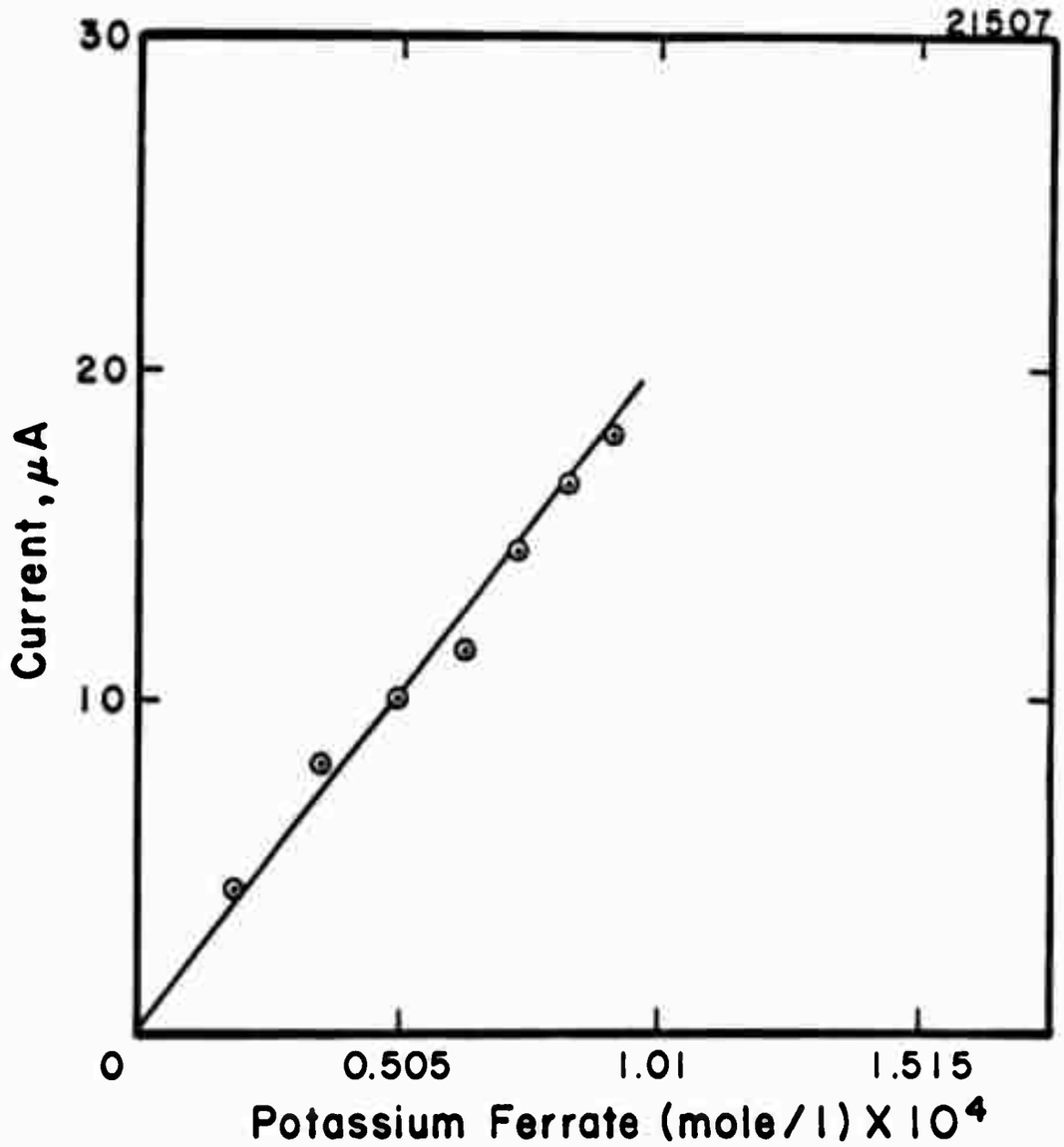

Figure 7. Calibration curve for potassium ferrate.

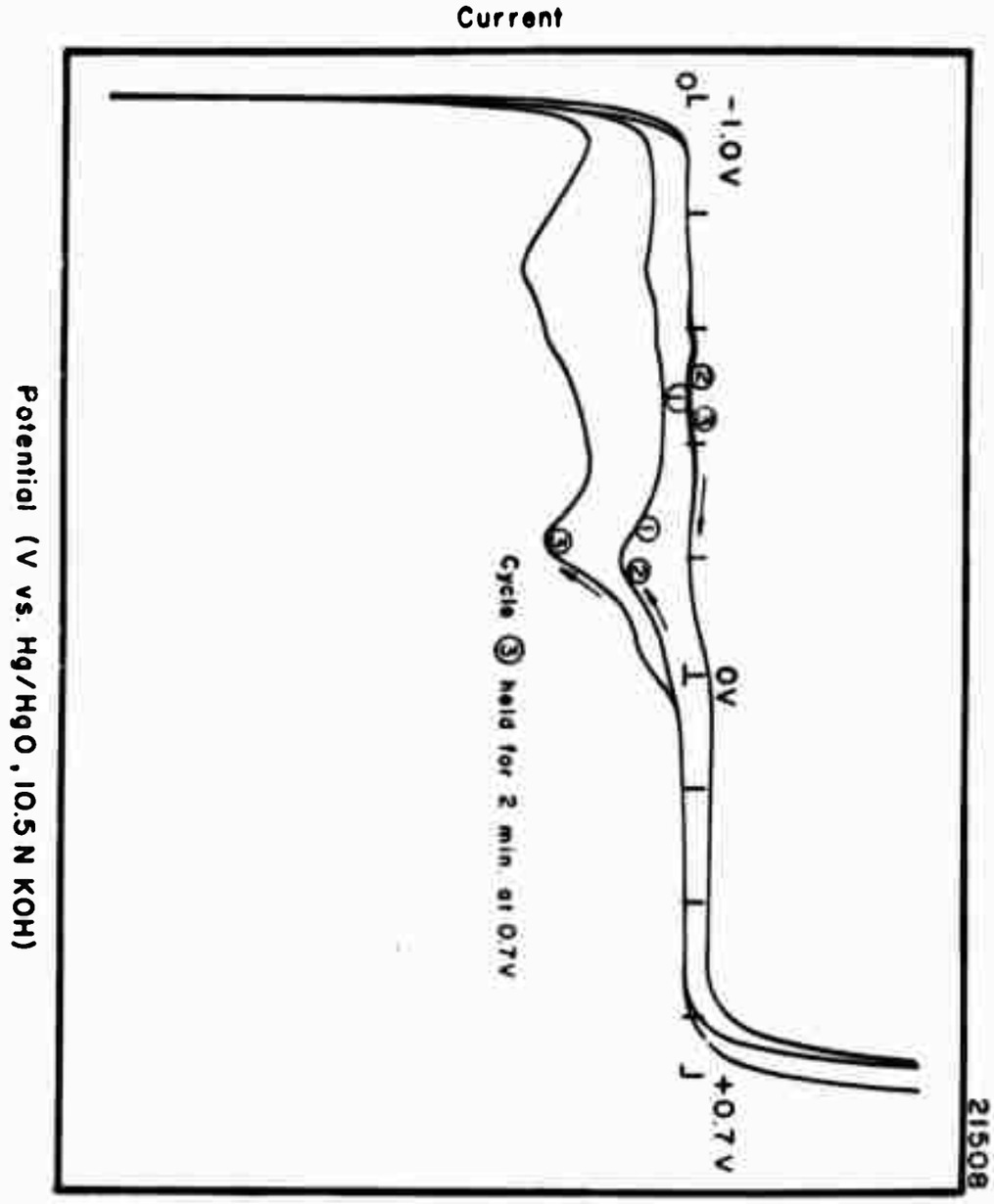

Figure 8. Voltammogram for 10.5N potassium hydroxide showing reduction of oxide film on platinum electrode at about -0.2V.

UNCLASSIFIED
Security Classification

AD 710331

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1 ORIGINATING ACTIVITY (Corporate author) UNIVERSITY OF KENTUCKY DEPARTMENT OF CHEMISTRY LEXINGTON, KENTUCKY	2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED 2b. GROUP

3 REPORT TITLE

FERRATE(VI) ANALYSIS BY SPECTROPHOTOMETRY AND VOLTAMMETRY

4 DESCRIPTIVE NOTES (Type of report and inclusive dates)

SCIENTIFIC - INTERIM

5 AUTHOR(S) (First name, middle initial, last name)

A. S. Venkatadri, W. F. Wagner and H. H. Bauer

6 REPORT DATE June 1970	7a. TOTAL NO. OF PAGES 17	7b. NO OF REFS 14
8a. CONTRACT OR GRANT NO. DAAB07-69-C-0366 b. PROJECT NO 170 c. 61102 d. B 81 A 00 071	9a. ORIGINATOR'S REPORT NUMBER(S) 12 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	

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11. SUPPLEMENTARY NOTES	12 SPONSORING MILITARY ACTIVITY PROJECT THEMIS(1002) U. S. Army Electronics Command ATTN: AMSEL-KL-PF, Dr. Wells Fort Monmouth, New Jersey 07703

13. ABSTRACT

Spectrophotometric and voltammetric methods were developed for the analysis of potassium ferrate(VI) in dilute solutions, where the standard chromite method is inapplicable. A direct proportionality prevails between the ferrate concentration and the absorbance on the one hand, and the ferrate concentration and the ferrate reduction current on the other. However, voltammetry has greater precision than spectrophotometry in very dilute solutions.

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14 KEY WORDS	LINK A		LINK B		LINK C	
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ferrate analysis						